

## WHAT IS CLAIMED IS:

1. A process of forming a HA/ZrO<sub>2</sub> complex coating on a Co-Cr-Mo alloy substrate, the Co-Cr-Mo substrate being subject to an electrolytic deposition sequentially in a ZrO(NO<sub>3</sub>)<sub>2</sub> bath and a mixed solution of Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and  
5 NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, and then the substrate being sintered to form the HA/ZrO<sub>2</sub> complex coating on the Co-Cr-Mo substrate.

2. The process of claim 1, wherein the electrolytic deposition of the Co-Cr-Mo substrate in the ZrO(NO<sub>3</sub>)<sub>2</sub> bath forms a Zr(OH)<sub>4</sub> colloidal layer on the Co-Cr-Mo substrate.

10 3. The process of claim 1, wherein the electrolytic deposition of the Co-Cr-Mo substrate in the mixed solution of Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> forms a Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> layer on the Zr(OH)<sub>4</sub> colloidal layer.

4. The process of claim 1, wherein the substrate having the Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> layer and the Zr(OH)<sub>4</sub> colloidal layer thereon is dried and sintered to form the HA/ZrO<sub>2</sub>  
15 complex coating.

5. The process of claim 1, wherein the concentration of the ZrO(NO<sub>3</sub>)<sub>2</sub> bath is the range of 0.0001M ~ 0.5M.

6. The process of claim 1, wherein the concentration of the ZrO(NO<sub>3</sub>)<sub>2</sub> bath is the range of 0.001M ~ 0.02M.

20 7. The process of claim 1, wherein the duration of electrolytic depositing the substrate in the ZrO(NO<sub>3</sub>)<sub>2</sub> bath is about 150s ~ about 3500s.

8. The process of claim 1, wherein the duration of electrolytic depositing the substrate in the ZrO(NO<sub>3</sub>)<sub>2</sub> bath is about 300s ~ about 2000s.

9. The process of claim 1, wherein the concentrations of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  in the mixed solution are respectively  $0.02\text{M} \sim 0.15\text{M}$  及  $0.005\text{M} \sim 0.5\text{M}$ .

10. The process of claim 1, wherein the concentrations of the  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  in the mixed solution are respectively  $0.04\text{M} \sim 0.1\text{M}$  and  $0.02\text{M} \sim$   
5 0.25M.

11. The process of claim 1, wherein the duration of electrolytic depositing the substrate in the mixed solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  is about  $100\text{s} \sim 3000\text{s}$ .

12. The process of claim 1, wherein the duration of electrolytic depositing the  
10 substrate in the mixed solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  is about  $500\text{s} \sim 2000\text{s}$ .

13. The process of claim 1, wherein voltage used for electrolytic depositing the substrate in the  $\text{ZrO}(\text{NO}_3)_2$  bath is about  $-0.6\text{ V} \sim -2.5\text{ V}$ .

14. The process of claim 1, wherein voltage used for electrolytic depositing the  
15 substrate in the  $\text{ZrO}(\text{NO}_3)_2$  bath is about  $-0.75\text{ V} \sim -1.1\text{ V}$ .

15. The process of claim 1, wherein voltage used for electrolytic depositing the substrate in the mixed solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  is about  $-0.5\text{ V} \sim -3\text{V}$ .

16. The process of claim 1, wherein voltage used for electrolytic depositing the  
20 substrate in the mixed solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  is about  $-0.6\text{ V} \sim -1.4\text{ V}$ .

17. The process of claim 1, wherein the substrate having the  $\text{Zr}(\text{OH})_4$  colloidal layer and the  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  layer thereon is slowly dried at constant temperature and humidity before sintered.

18. The process of claim 1, wherein the substrate is further dried at temperature of about 15 ~ 40°C and relative humidity of more than 75% before sintered.

19. The process of claim 1, wherein the sintering temperature is not high than 500°C.

5           20. The process of claim 1, wherein the sintering temperature is raised at stages, the temperature changing rate is not quick, and the temperature is kept for a while between two temperature changing stages.

21. The process of claim 20, wherein the temperature is raised at 2°C/min at each temperature changing stage.

10           22. A process of forming a HA/ZrO<sub>2</sub> complex coating on a Co-Cr-Mo alloy substrate, the Co-Cr-Mo substrate being subjected to an electrolytic deposition sequentially in a ZrO(NO<sub>3</sub>)<sub>2</sub> bath and a mixed solution of Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, then the substrate being slowly dried, and the substrate being sintered at a temperature not higher than 500°C to form the HA/ZrO<sub>2</sub> complex coating on the  
15 Co-Cr-Mo substrate, wherein the sintering temperature is raised at several temperature stages.

23. The process of claim 22, wherein the electrolytic deposition of the Co-Cr-Mo substrate in the ZrO(NO<sub>3</sub>)<sub>2</sub> bath forms a Zr(OH)<sub>4</sub> colloidal layer on the Co-Cr-Mo substrate.

20           24. The process of claim 22, wherein the electrolytic deposition of the Co-Cr-Mo substrate in the mixed solution of Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> forms a Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> layer on the Zr(OH)<sub>4</sub> colloidal layer.

25. The process of claim 22, wherein the substrate having the  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  layer and the  $\text{Zr}(\text{OH})_4$  colloidal layer thereon is dried and sintered to form the HA/ $\text{ZrO}_2$  complex coating.

26. The process of claim 22, wherein the concentration of the  $\text{ZrO}(\text{NO}_3)_2$  bath is  
5 the range of 0.0001M ~ 0.5M.

27. The process of claim 22, wherein the concentration of the  $\text{ZrO}(\text{NO}_3)_2$  bath is the range of 0.001M ~ 0.02M.

28. The process of claim 22, wherein the duration of electrolytic depositing the substrate in the  $\text{ZrO}(\text{NO}_3)_2$  bath is about 150s ~ about 3500s.

10 29. The process of claim 22, wherein the duration of electrolytic depositing the substrate in the  $\text{ZrO}(\text{NO}_3)_2$  bath is about 300s ~ about 2000s.

30. The process of claim 22, wherein the concentrations of the  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  in the mixed solution are respectively 0.02M~0.15M 及 0.005M~  
0.5M .

15 31. The process of claim 22, wherein the concentrations of the  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  in the mixed solution are respectively 0.04M ~ 0.1M and 0.02M ~  
0.25M.

32. The process of claim 22, wherein the duration of electrolytic depositing the substrate in the mixed solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  is about 100s ~  
20 3000s.

33. The process of claim 22, wherein the duration of electrolytic depositing the substrate in the mixed solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  is about 500s ~  
2000s.

34. The process of claim 22, wherein voltage used for electrolytic depositing the substrate in the  $\text{ZrO}(\text{NO}_3)_2$  bath is about  $-0.6 \text{ V} \sim -2.5 \text{ V}$ .

35. The process of claim 22, wherein voltage used for electrolytic depositing the substrate in the  $\text{ZrO}(\text{NO}_3)_2$  bath is about  $-0.75 \text{ V} \sim -1.1 \text{ V}$ .

5        36. The process of claim 22, wherein voltage used for electrolytic depositing the substrate in the mixed solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  is about  $-0.5 \text{ V} \sim -3\text{V}$ .

37. The process of claim 22, wherein voltage used for electrolytic depositing the substrate in the mixed solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  is about  $-0.6 \text{ V} \sim$   
10     $-0.4 \text{ V}$ .

38. The process of claim 22, wherein the substrate having the  $\text{Zr}(\text{OH})_4$  colloidal layer and the  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  layer thereon is slowly dried at constant temperature and humidity before sintered.

39. The process of claim 22, wherein the substrate is further dried at temperature  
15    of about  $15 \sim 40^\circ\text{C}$  and relative humidity of more than 75% before sintered.